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(54) Title: FOAMED THERMOPLASTIC POLYURETHANES

(57) Abstract: Process for the preparation of foamed thermoplastic polyurethanes characterised in that the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres and a plasticizer.

FOAMED THERMOPLASTIC POLYURETHANES

Field of the invention

The present invention is concerned with a process for the preparation of foamed thermoplastic polyurethanes, novel foamed thermoplastic polyurethanes and reaction systems for preparing foamed thermoplastic polyurethanes.

Background of the invention

Thermoplastic polyurethanes, herein after referred to as TPUs, are well-known thermoplastic elastomers. In particular, they exhibit very high tensile and tear strength, high flexibility at low temperatures, extremely good abrasion and scratch resistance. They also have a high stability against oil, fats and many solvents, as well as stability against UV radiation and are being employed in a number of end use applications such as the automotive and the footwear industry.

As a result of the increased demand for lighter materials, a low density TPU needs to be developed which, in turn, represents a big technical challenge to provide, at minimum, equal physical properties to conventional low density PU.

It is already known to produce soles and other parts of polyurethane by a polyaddition reaction of liquid reactants resulting in an elastic solid moulded body. Up till now the reactants used were polyisocyanates and polyesters or polyethers containing OH-groups. Foaming was effected by adding a liquid of low boiling point or by means of CO_2, thereby obtaining a foam at least partially comprising open cells.

Reducing the weight of the materials by foaming the TPU has not given satisfactory results up to now. Attempts to foam TPU using well-known blowing agents as azodicarbonamides (exothermic) or sodiumhydrocarbonate (endothermic) based products were not successful for mouldings with reduced densities below 800 kg/m^3.

With endothermic blowing agents, a good surface finish can be obtained but the lowest density achievable is about 800 kg/m^3. Also, the processing is not very consistent and results in long demoulding times. Very little or no foaming is obtained at the mould surface due to a relatively low mould temperature, resulting in a compact, rather thick skin and a coarse cell core.

By using exothermic blowing agents, a lower density foam (down to 750 kg/m^3) with very fine cell structure can be achieved but the surface finish is not acceptable for most applications and demould time is even longer.

From the above it is clear that there is a continuous demand for low density TPUs having improved skin quality which can be produced with reduced demould times.

It has now been surprisingly found that foaming TPUs in the presence of thermally expandable microspheres and a plasticizer, allows to meet the above objectives. Demould times are significantly reduced and the process can be carried out at lower temperatures, resulting in a better barrel stability. In addition, the use of microspheres and a plasticizer even allows to further reduce the density while maintaining or improving the skin quality and demould time.

The present invention thus concerns a process for the preparation of foamed thermoplastic polyurethanes whereby the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres and a plasticizer.

The low density thermoplastic polyurethanes thus obtained (density not more than 800 kg/m^3) have a fine cell structure, very good surface appearance, a relatively thin skin and show comparable physical properties to conventional PU which renders them suitable for a wide variety of applications.

The invention provides TPU products having outstanding low temperature dynamic flex properties and green strength at the time of demould, at density 800 kg/m^3 and below.

The term "green strength", as is known in the art, denotes the basic integrity and strength of the TPU at demould. The polymer skin of a moulded item, for example, a shoe sole and other moulded articles, should possess sufficient tensile strength and elongation and tear strength to survive a 90 to 180 degree bend without exhibiting surface cracks. The prior art processes often require 5 minutes minimum demould time to attain this characteristic.

In addition, the present invention therefore provides a significant improvement in minimum demould time. That is to say, a demould time of 2 to 3 minutes is achievable.

The use of microspheres in a polyurethane foam has been described in EP-A 29021 and US-A 5418257.

Adding blowing agents during the processing of TPUs is widely known, see e.g. WO-A 94/20568, which discloses the production of foamed TPUs, in particular expandable, particulate TPUs, EP-A 516024, which describes the production of foamed sheets from TPU by mixing with a blowing agent and heat-processing in an extruder, and DE-A 4015714, which concerns glass-fibre reinforced TPUs made by injection moulding TPU mixed with a blowing agent.

Nevertheless, none of the prior art documents discloses the use of thermally expandable microspheres and a plasticizer to improve the skin quality of foamed low density TPU (density 800 kg/m^3 and even below) nor do these documents suggest the benefits associated with the present invention.

It has also been found that the plasticizer of the present invention allows an improved density reduction obtained by the microspheres while at the same time improving the cell structure. In addition more soft and flexible end product with excellence performance characteristics is obtained.

Detailed description

Thermoplastic polyurethanes are obtainable by reacting a difunctional isocyanate composition with at least one difunctional polyhydroxy compound and optionally a chain

extender in such amounts that the isocyanate index is between 90 and 110, preferably between 95 and 105, and most preferably between 98 and 102.

The term 'difunctional' as used herein means that the average functionality of the isocyanate composition and the polyhydroxy compound is about 2.

The term "isocyanate index" as used herein is the ratio of isocyanate-groups over isocyanate-reactive hydrogen atoms present in a formulation, given as a percentage. In other words, the isocyanate index expresses the percentage of isocyanate actually used in a formulation with respect to the amount of isocyanate theoretically required for reacting with the amount of isocyanate-reactive hydrogen used in a formulation.

It should be observed that the isocyanate index as used herein is considered from the point of view of the actual polymer forming process involving the isocyanate ingredient and the isocyanate-reactive ingredients. Any isocyanate groups consumed in a preliminary step to produce modified polyisocyanates (including such isocyanate-derivatives referred to in the art as quasi- or semi-prepolymers) or any active hydrogens reacted with isocyanate to produce modified polyols or polyamines, are not taken into account in the calculation of the isocyanate index. Only the free isocyanate groups and the free isocyanate-reactive hydrogens present at the actual elastomer forming stage are taken into account.

The difunctional isocyanate composition may comprise any aliphatic, cycloaliphatic or aromatic isocyanates. Preferred are isocyanate compositions comprising aromatic diisocyanates and more preferably diphenylmethane diisocyanates.

The polyisocyanate composition used in the process of the present invention may consist essentially of pure 4,4'-diphenylmethane diisocyanate or mixtures of that diisocyanate with one or more other organic polyisocyanates, especially other diphenylmethane diisocyanates, for example the 2,4'-isomer optionally in conjunction with the 2,2'-isomer. The polyisocyanate component may also be an MDI variant derived from a polyisocyanate composition containing at least 95% by weight of 4,4'-diphenylmethane diisocyanate. MDI variants are well known in the art and, for use in accordance with the invention,

particularly include liquid products obtained by introducing carbodiimide groups into said polyisocyanate composition and/or by reacting with one or more polyols.
Preferred polyisocyanate compositions are those containing at least 80% by weight of 4,4'-diphenylmethane diisocyanate. More preferably, the 4,4'- diphenylmethane diisocyanate content is at least 90, and most preferably at least 95% by weight.

The difunctional polyhydroxy compound used has a molecular weight of between 500 and 20000 and may be selected from polyesteramides, polythioethers, polycarbonates, polyacetals, polyolefins, polysiloxanes, polybutadienes and, especially, polyesters and polyethers, or mixtures thereof. Other dihydroxy compounds such as hydroxyl-ended styrene block copolymers like SBS, SIS, SEBS or SIBS may be used as well.

Mixtures of two or more compounds of such or other functionalities and in such ratios that the average functionality of the total composition is about 2 may also be used as the difunctional polyhydroxy compound. For polyhydroxy compounds the actual functionality may e.g. be somewhat less than the average functionality of the initiator due to some terminal unsaturation. Therefore, small amounts of trifunctional polyhydroxy compounds may be present as well in order to achieve the desired average functionality of the composition.

Polyether diols which may be used include products obtained by the polymerisation of a cyclic oxide, for example ethylene oxide, propylene oxide, butylene oxide or tetrahydrofuran in the presence, where necessary, of difunctional initiators. Suitable initiator compounds contain 2 active hydrogen atoms and include water, butanediol, ethylene glycol, propylene glycol, diethylene glycol, triethylene glycol, dipropylene glycol, 1,3-propane diol, neopentyl glycol, 1,4-butanediol, 1,5-pentanediol, 1,6-pentanediol and the like. Mixtures of initiators and/or cyclic oxides may be used.

Especially useful polyether diols include polyoxypropylene diols and poly(oxyethylene-oxypropylene) diols obtained by the simultaneous or sequential addition of ethylene or propylene oxides to difunctional initiators as fully described in the prior art. Random copolymers having oxyethylene contents of 10-80%, block copolymers having oxyethylene contents of up to 25% and random/block copolymers having oxyethylene contents of up to

50%, based on the total weight of oxyalkylene units, may be mentioned, in particular those having at least part of the oxyethylene groups at the end of the polymer chain. Other useful polyether diols include polytetramethylene diols obtained by the polymerisation of tetrahydrofuran. Also suitable are polyether diols containing low unsaturation levels (i.e. less than 0.1 milliequivalents per gram diol).

Other diols which may be used comprise dispersions or solutions of addition or condensation polymers in diols of the types described above. Such modified diols, often referred to as 'polymer' diols have been fully described in the prior art and include products obtained by the in situ polymerisation of one or more vinyl monomers, for example styrene and acrylonitrile, in polymeric diols, for example polyether diols, or by the in situ reaction between a polyisocyanate and an amino- and/or hydroxyfunctional compound, such as triethanolamine, in a polymeric diol.

Polyoxyalkylene diols containing from 5 to 50% of dispersed polymer are useful as well. Particle sizes of the dispersed polymer of less than 50 microns are preferred.

Polyester diols which may be used include hydroxyl-terminated reaction products of dihydric alcohols such as ethylene glycol, propylene glycol, diethylene glycol, 1,4-butanediol, neopentyl glycol, 2-methylpropanediol, 3-methylpentane-1,5-diol, 1,6-hexanediol or cyclohexane dimethanol or mixtures of such dihydric alcohols, and dicarboxylic acids or their ester-forming derivatives, for example succinic, glutaric and adipic acids or their dimethyl esters, sebacic acid, phthalic anhydride, tetrachlorophthalic anhydride or dimethyl terephthalate or mixtures thereof.

Polyesteramides may be obtained by the inclusion of aminoalcohols such as ethanolamine in polyesterification mixtures.

Polythioether diols which may be used include products obtained by condensing thiodiglycol either alone or with other glycols, alkylene oxides, dicarboxylic acids, formaldehyde, amino-alcohols or aminocarboxylic acids.

Polycarbonate diols which may be used include those prepared by reacting glycols such as diethylene glycol, triethylene glycol or hexanediol with formaldehyde. Suitable polyacetals may also be prepared by polymerising cyclic acetals.

Suitable polyolefin diols include hydroxy-terminated butadiene homo- and copolymers and suitable polysiloxane diols include polydimethylsiloxane diols.

Suitable difunctional chain extenders include aliphatic diols, such as ethylene glycl, 1,3-propanediol, 1,4-butanediol, 1,5-pentanediol, 1,6-hexanediol, 1,2-propanediol, 2-methylpropanediol, 1,3-butanediol, 2,3-butanediol, 1,3-pentanediol, 1,2-hexanediol, 3-methylpentane-1,5-diol, diethylene glycol, dipropylene glycol and tripropylene glycol, and aminoalcohols such as ethanolamine, N-methyldiethanolamine and the like. 1,4-butanediol is preferred.

The TPUs suitable for processing according to the invention can be produced in the so-called one-shot, semi-prepolymer or prepolymer method, by casting, extrusion or any other process known to the person skilled in the art and are generally supplied as granules or pellets.

Optionally, small amounts, i.e. up to 30, preferably 20 and most preferably 10, wt% based on the total of the blend, of other conventional thermoplastic elastomers such as PVC, EVA, TR or mixtures thereof may be blended with the TPU.

Any thermally expandable microspheres can be used in the present invention. However, microspheres containing hydrocarbons, in particular aliphatic or cycloaliphatic hydrocarbons, are preferred.

The term "hydrocarbon" as used herein is intended to include non-halogenated and partially or fully halogenated hydrocarbons.

Thermally expandable microspheres containing a (cyclo)aliphatic hydrocarbon, which are particularly preferred in the present invention, are commercially available. These include expanded and unexpanded microspheres. Preferred microspheres are unexpanded or

partially unexpanded microspheres consisting of small spherical particles with an average diameter of typically 10 to 15 micron. The sphere is formed of a gas proof polymeric shell (consisting e.g. of acrylonitrile or PVDC), encapsulating a minute drop of a (cyclo)aliphatic hydrocarbon, e.g. liquid isobutane. When these microspheres are subjected to heat at an elevated temperature level (e.g. 150°C to 200°C) sufficient to soften the thermoplastic shell and to volatilize the (cyclo)aliphatic hydrocarbon encapsulated therein, the resultant gas expands the shell and increases the volume of the microspheres. When expanded, the microspheres have a diameter 3.5 to 4 times their original diameter as a consequence of which their expanded volume is about 50 to 60 times greater than their initial volume in the unexpanded state. An example of such microspheres are the EXPANCEL-DU microspheres which are marketed by AKZO Nobel Industries of Sweden ('EXPANCEL' is a trademark of AKZO Nobel Industries).

Another essential ingredient is a plasticizer. The plasticizer is typically present in an amount between 0.1 to 60%, more preferably more than 20% by weight of the TPU.

The plasticizer suitable in the preparation of the composition of the present invention include the plasticizers as described in US 5,908,894. Preferred plasticizers include phthalates, such as benzyl phthalate and dioctyl phthalate, and esters of sebacic acid or adipic acid. In particular benzyl butyl phthalate, is highly preferred. Other preferred plasticizers are non-phtalate containing plasticizers such as adipates.

In a preferred embodiment, a blowing agent is added to the system, which may either be an exothermic or endothermic blowing agent, or a combination of both. Most preferably however, an endothermic blowing agent is added.

Any known blowing agent used in the preparation of foamed thermoplastics may be used in the present invention as blowing agents.

Examples of suitable chemical blowing agents include gaseous compounds such as nitrogen or carbon dioxide, gas (e.g. CO_2) forming compounds such as azodicarbonamides, carbonates, bicarbonates, citrates, nitrates, borohydrides, carbides such as alkaline earth and alkali metal carbonates and bicarbonates e.g. sodium bicarbonate and

sodium carbonate, ammonium carbonate, diaminodiphenylsulphone, hydrazides, malonic acid, citric acid, sodium monocitrate, ureas, azodicarbonic methyl ester, diazabicylooctane and acid/carbonate mixtures or mixtures thereof.
Preferrd endothermic blowing agents comprise bicarbonates and/or citrates.

Examples of suitable physical blowing agents include volatile liquids such as chlorofluorocarbons, partially halogenated hydrocarbons or non-halogenated hydrocarbons like propane, n-butane, isobutane, n-pentane, isopentane and/or neopentane.

Preferred endothermic blowing agents are the so-called 'HYDROCEROL' blowing agents as disclosed in a.o. EP-A 158212 and EP-A 211250, which are known as such and commercially available ('HYDROCEROL' is a trademark of Clariant).

Azodicarbonamide type blowing agents are preferred as exothermic blowing agents.

Microspheres are usually used in amount of from 0.05 to 10.0 parts, preferably from 0.1 to 5.0 part, by weight per 100 parts by weight of thermoplastic polyurethane. From 0.5 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane of microspheres are preferred. Most preferably, microspheres are added in amounts from 1.0 to 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

The total amount of blowing agent added is usually from 0.01 to 15.0, preferably from 0.1 to 5.0 parts by weight per 100 parts by weight of thermoplastic polyurethane. Preferably, from 0.5 to 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane of blowing agent is added. Most preferably, blowing agent is added in amounts from 1.0 to 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

Additives which are conventionally used in thermoplastics processing may also be used in the process of the present invention. Such additives include catalysts, for example tertiary amines and tin compounds, surface-active agents and foam stabilisers, for example siloxane-oxyalkylene copolymers, flame retardants, antistatic agents, flow aids, organic and inorganic fillers, pigments and internal mould release agents.

The foamed thermoplastic polyurethanes of the present invention can be made via a variety of processing techniques, such as extrusion, calendering, thermoforming, flow moulding or injection moulding. Injection moulding is however the preferred production method.
The presence of thermally expandable microspheres allows for a reduction in processing temperatures. Typically the process of the present invention is carried out at temperatures between 150 and 175°C.

Advantageously, the mould is pressurised, preferably with air, and the pressure is released during foaming. Although such process is known and commonly available from several machine producers, it has been surprisingly found that conducting the process of the present invention in a pressurised mould results in TPU articles having an excellent surface finish and physical properties, while having an even further reduced density (down to 350 kg/m^3).

Thermoplastic polyurethanes of any density between about 100 and 1200 kg/m^3 can be prepared by the method of this invention, but it is primarily of use for preparing foamed thermoplastic polyurethanes having densities of less than 800 kg/m^3, more preferably less than 700 kg/m^3 and most preferably less than 600 kg/m^3.

The thermally expandable microspheres can also be successfully used it produce TPU hardnesses from 50 Shore to 60 Shore D. The TPU hardness can be adjusted by changing the ratio of isocyanate and chain extender (hard block) to polyol (soft block) and/or the addition of plasticizer.

The thermoplastic polyurethane is customarily manufactured as pellets for later processing into the desired article. The term 'pellets' is understood and used herein to encompass various geometric forms, such as squares, trapezoids, cylinders, lenticular shapes, cylinders with diagonal faces, chunks, and substantially spherical shapes including a particle of powder or a larger-size sphere. While thermoplastic polyurethanes are often sold as pellets, the polyurethane could be in any shape or size suitable for use in the equipment used to form the final article.

According to another embodiment of the present invention, the thermoplastic polyurethane pellet of the present invention comprises a thermoplastic polyurethane body, the thermally expandable microspheres and a binding agent which binds the body and the microspheres. The binding agent comprises a polymeric component that has an onset temperature for its melt processing lower than the onset temperature of the melt processing range of the TPU. The pellets may also include blowing agents and/or additive components such as colorant, pigments, flow aids, antistatic agents, plasticizers, microbiocides.

The binding agent covers at least part of the thermoplastic polyurethane body. In a preferred embodiment, the thermoplastic polyurethane body and microspheres are substantially encapsulated by the binding agent. By 'substantially encapsulated' we mean that at least three-quarters of the surface of the thermoplastic polyurethane body is coated, and preferably at least about nine-tenths of the resin body is coated. It is particularly preferred for the binding agent to cover substantially all of the polyurethane body and microspheres. The amount of binding agent to the thermoplastic polyurethane may typically range from at least about 0.1% by weight and up to about 10% by weight, based on the weight of the thermoplastic polyurethane pellet. Preferably, the amount of the binding agent is at least about 0.5% by weight and up to 5% by weight, based on the weight of the thermoplastic polyurethane pellet.

Preferably, the binding agent has an onset temperature for its melt processing range that is below the onset temperature of the melt processing range of the thermoplastic polyurethane body. Thus the binding agent may be applied as a melt to the thermoplastic polyurethane body composition while the latter is a solid or substantially a solid. The onset temperature of the melt processing range ot the binding agent is preferably above about 20 degree C, and more preferably it is above 60 degree C, and even more preferably it is at least about 80 degree C. The onset temperature of the melt processing range of the polymeric component of the coating preferably has an onset temperature for its melt processing range at least about 20 degree C and even more preferably at least about 40 degree C. below, the onset temperature for the melt processing range of the thermoplastic polyurethane body. If the customized thermoplastic polyurethane pellets are to be dried using a dryer, then the melt processing range of the binding agent is preferably above the temperature of the

dryer. In a preferred embodiment, the binding agent is chosen to prevent or slow water absorption so that a drying step before forming the desired article is unnecessary.

The binding agent may then be added to the TPU pellets by several different methods. In one method, the pellets are placed in a container with the coating composition while the pellets are still at a temperature above the onset temperature of the melt processing range of the binding agent. In this case the binding agent may be already melted or may be melted by the heat of the pellets or by heat applied externally to the container. For example, without limitation, the binding agent may be introduced to the container as a powder when it is to be melted in the container. The binding agent can be any substance capable of binding the thermoplastic polyurethane body and the microspheres. Preferably the binding agent comprises a polymeric component. Examples of suitable polymeric components include polyisocyanates and/or prepolymers thereof.

The foamed thermoplastic polyurethanes obtainable via the process of the present invention are particularly suitable for use in any application of thermoplastic rubbers including, for example, footwear or integral skin applications like steering wheels.

Customized thermoplastic polyurethanes may be produced more efficiently using the process according to the present invention. The customized thermoplastic polyurethanes may be formed into any of the articles generally made with thermoplastic resins. Examples of articles are interior and exterior parts of automobiles, such as inside panels, bumpers, housing of electric devices such as television, personal computers, telephones, video cameras, watches, note-book personal computers; packaging materials; leisure goods; sporting goods and toys.

The compositions according to the present invention can also be blended with other polymers ,PVC, styrenic polymers (polymers which contain styrene, such as acrylonitrile-styrene-acrylate (ASA) polymers), polyolefins and polyamides to produce compositions which exhibit good overall characteristics. Such polymeric compositions can be especially used in manufacturing a wide variety of useful articles, such as profiles, moldings, sheeting, flooring, wall coverings, hose, cables and footwear. The thermoplastic polyurethanes of the present invention can also be blended with other polymers to produce

compositions which feel soft to the touch and exhibit good adhesion properties onto thermoplastics, such as ABS PMMA, ASA, PC and the like. Such blends can be utilized in a wide variety of applications including coatings.

In another embodiment, the present invention concerns a reaction system comprising (a) a TPU and (b) thermally expandable microspheres.

The invention is illustrated, but not limited, by the following examples in which all parts, percentages and ratios are by weight.

Example 1 (comparative)

TPU pellets (Avalon 65AE; 'Avalon' is a trademark of Huntsman ICI Chemicals, LLC) were dry blended with 2% of thermally expandable microspheres (Expancel 092 MB120). The dry blend was then processed on an injection moulding machine (Desma SPE 231) to form a test moulding of dimensions 19.5 *12.0 * 1 cm.

The processing temperatures for all the examples can be seen on Table 1. The physical properties obtained for all the examples can be seen on Table 2. Abrasion was measured according to DIN53516.

Example 2 (comparative)

TPU pellets (Avalon 65AE; 'Avalon' is a trademark of Huntsman ICI Chemicals, LLC) were dry blended with an exothermic blowing agent (Celogen AZNP130; available from Uniroyal) with 2% of thermally expandable microspheres (Expancel 092 MB120). The dry blend was then processed on an injection moulding machine (Desma SPE 231) to form a test moulding of dimensions 19.5 *12.0 * 1 cm.

The processing temperatures for all the examples can be seen on Table 1. The physical properties obtained for all the examples can be seen on Table 2. Abrasion was measured according to DIN53516.

Example 3

The same as comparative example 1 except for the extra addition of 40% of benzyl butyl phthalate.

Example 4

The same as comparative example 2 except for the extra addition of 40% of benzyl butyl phthalate.

Table 1 : Processing Temperatures of Injection Moulding

	Zone 1	Zone 2	Zone 3	Nozzle	Mould Temp.(C)
Ex.1*	160	165	170	165	50
Ex.2*	160	165	170	165	50
Ex.3	160	165	170	165	50
Ex.4	160	165	170	165	50

* : comparative example

Table 2 : Properties

	Density (kg/m^3)	**Hardness (Shore A)**	**Abrasion (mg)**	**Flex. Resistance (No. of cycles)**	**Demould time (seconds)**	**Cell structure**
Ex.1*	750	61	70	>100.000	210	Good
Ex.2*	750	61	70	>100.000	210	Good
Ex.3	750	61	70	>100.000	210	Excellent
Ex.4	750	61	70	>100.000	210	Excellent

* : comparative example

Claims

1. Process for the preparation of foamed thermoplastic polyurethanes characterised in that the foaming of the thermoplastic polyurethane is carried out in the presence of thermally expandable microspheres and a plasticizer wherein the amount of plasticizer is more than 20% by weight of the thermoplastic polyurethane.

2. Process according to claim 1 wherein the thermally expandable microspheres contain a hydrocarbon.

3. Process according to claim 2 wherein the hydrocarbon is an aliphatic or cycloaliphatic hydrocarbon.

4. Process according to claims 1-3 wherein said plasticizer is a phthalates .

5. Process according to any of the preceding claims wherein an endothermic blowing agent is present.

6. Process according to any of the preceding claims wherein an exothermic blowing agent is present.

7. Process according to claim 5 or 6 wherein the endothermic blowing agent comprises bicarbonates or citrates.

8. Process according to any of claims 6 - 7 wherein the exothermic blowing agent comprises azodicarbonamide type compounds.

9. Process according to any of the preceding claims which is carried out by injection moulding.

10. Process according to any of the preceding claims which is carried out in a mould pressurized with air.

11. Process according to any of the preceding claims wherein the starting thermoplastic polyurethane is made by using a difunctional isocyanate composition comprising an aromatic difunctional isocyanate.

12. Process according to claim 11 wherein the aromatic difunctional isocyanate comprises diphenylmethane diisocyanate.

13. Process according to claim 12 wherein the diphenylmethane diisocyanate comprises at least 80% by weight of 4,4'-diphenylmethane diisocyanate.

14. Process according to any of the preceding claims wherein the difunctional polyhydroxy compound comprises a polyoxyalkylene diol or polyester diol.

15. Process according to claim 14 wherein the polyoxyalkylene diol comprises oxyethylene groups.

16. Process according to claim 15 wherein the polyoxyalkylene diol is a poly(oxyethylene-oxypropylene) diol.

17. Process according to any of the preceding claims wherein the amount of microspheres is between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

18. Process according to claim 17 wherein the amount of microspheres is between 1.0 and 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

19. .Process according to any of claims 5-18 wherein the amount of blowing agent is between 0.5 and 4.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

20. Process according to claim 19 wherein the amount of blowing agent is between 1.0 and 3.0 parts by weight per 100 parts by weight of thermoplastic polyurethane.

21. Foamed thermoplastic polyurethane obtainable by reacting a difunctional isocyanate composition with at least one difunctional polyhydroxyl polyhydroxy compound, in the presence of thermally expandable microspheres, and in the presence of a a plasticizer where the amount of plasticizer is more than 20% by weight of the thermoplastic polyurethane, said polyurethane having a density of not more than 700 kg/ m^3..

22. Foamed thermoplastic polyurethane according to claim 21 having a density of not more than 600 kg/m^3 .

23. Reaction system comprising :

a) TPU
b) thermally expandable microspheres
c) a plasticizer being present by more than 20% by weight of the TPU

INTERNATIONAL SEARCH REPORT	International Application No PCT/EP 01/06897

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C08J9/32 C08J9/00 //C08L75/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 272 001 A (WEISMAN MOREY) 21 December 1993 (1993-12-21) column 5, line 4-60 claims ---	1-23
Y	WO 99 61216 A (MAGNA INTERIOR SYSTEMS INC) 2 December 1999 (1999-12-02) page 12, line 22-26 page 13, line 7-14 ---	1-23
X,P	WO 00 44821 A (LIMERKENS DOMINICUS ;EDOM BART VAN (BE); DIJCK JOHAN VAN (BE); WAT) 3 August 2000 (2000-08-03)	21,22
A	page 6, line 17-23 page 9, line 26 claims ---	1-20,23
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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
5 November 2001	05/10/2001

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Oudot, R

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International Application No
PCT/EP 01/06897

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Section Ch, Week 199835 Derwent Publications Ltd., London, GB; Class A25, AN 1998-408782 XP002153120 & JP 10 168215 A (SEKISUI PLASTICS CO LTD) , 23 June 1998 (1998-06-23) abstract ---	21,22
A	GB 1 388 748 A (UNION CARBIDE CORP) 26 March 1975 (1975-03-26) page 6, line 28-41 page 6, line 60-65 claims ---	1-23
A	EP 0 692 516 A (BURGER HANS JOACHIM) 17 January 1996 (1996-01-17) claims ---	1-23
A	EP 0 401 982 A (HOOVER UNIVERSAL) 12 December 1990 (1990-12-12) claims -----	10

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 5

Claim 5:
"Process according to claims 1-4 wherein SAID flow aid is present in an amount from 0,1 % to 10 % by weight of the TPU".
This compound has not been introduced in any of claims 1-4.
No compound defined as "flow aid" has been indicated neither in the description of the invention nor in the examples.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 01/06897

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
US 5272001	A	21-12-1993	US	5332760 A	26-07-1994
			US	5418257 A	23-05-1995
WO 9961216	A	02-12-1999	AU	3805599 A	13-12-1999
			BR	9910600 A	16-01-2001
			WO	9961216 A1	02-12-1999
			CN	1302250 T	04-07-2001
			EP	1079962 A1	07-03-2001
WO 0044821	A	03-08-2000	AU	2796100 A	18-08-2000
			WO	0044821 A1	03-08-2000
JP 10168215	A	23-06-1998	NONE		
GB 1388748	A	26-03-1975	CA	980491 A1	23-12-1975
			JP	48025097 A	02-04-1973
EP 0692516	A	17-01-1996	EP	0692516 A1	17-01-1996
EP 0401982	A	12-12-1990	CA	2016270 A1	08-12-1990
			EP	0401982 A2	12-12-1990